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• Slack, William E.  
Moundsville, WV 2604 (US)  
• Squiller, Edward P.  
Pittsburgh, PA 15205 (US)

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(74) Representative:  
Steiling, Lothar, Dr.  
Bayer AG  
Konzernbereich RP  
Patente und Lizenzen  
51368 Leverkusen (DE)

(71) Applicant: Bayer Corporation  
Pittsburgh, PA 15205-9741 (US)

(72) Inventors:

• Yeske, Philip E.  
51061 Köln (DE)

### (54) Low surface energy polyisocyanates and their use in one- or two-component coating compositions

(57) The present invention relates to polyisocyanate adducts containing allophanate groups, fluorine and optionally isocyanurate groups that are prepared by reacting compounds a) which

- i) are substantially free of hydroxyl groups and isocyanate groups,
- ii) have an average of at least two urethane groups per molecule and
- iii) contain 0 to 50% by weight of fluorine, based on the weight of the polyisocyanate adducts,

with an excess quantity, based on the equivalents of urethane groups, of polyisocyanates b), which optionally contain fluorine, to form polyisocyanate adducts and optionally removing at least a portion of the unreacted excess polyisocyanates b), provided that compounds a) and polyisocyanates b) contain a total of at least 0.001% by weight, of fluorine, based on the weight of the polyisocyanate adducts.

The present invention also relates to a process for preparing these polyisocyanates adducts, to blends of the polyisocyanate adducts with other polyisocyanates that do not contain fluorine and to the use of the polyisocyanate adducts or polyisocyanate blends, optionally in blocked form, in one- or two-component coating compositions.

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- ii) have an average of at least two urethane groups per molecule and
- iii) contain 0 to 50% by weight of fluorine, based on the weight of the polyisocyanate adducts,

with an excess quantity, based on the equivalents of urethane groups, of polyisocyanates, which optionally contain fluorine, to form the polyisocyanate adducts and optionally removing at least a portion of the unreacted excess polyisocyanates, provided that compounds a) and polyisocyanates b) contain a total of at least 0.001% by weight, of fluorine, based on the weight of the polyisocyanate adducts.

Finally, the present invention also relates to blends of these polyisocyanate adducts with other polyisocyanates that do not contain fluorine and to the use of the polyisocyanate adducts or polyisocyanate blends, optionally in blocked form, in one- or two-component coating compositions.

#### DETAILED DESCRIPTION OF THE INVENTION

Starting materials for the process according to the invention are compounds a) containing urethane groups and optionally fluorine and polyisocyanates b), preferably diisocyanates, which optionally contain fluorine, provided that at least one of these components contain fluorine. The two starting components are reacted together to form polyisocyanates containing allophanate groups, fluorine and optionally isocyanurate groups.

Compounds a) have an average of at least two urethane groups per molecule and a number average molecular weight, which may be calculated from the stoichiometry of the starting materials, of less than 10,000, preferably less than 5000 and more preferably less than 3000. The compounds are substantially free of isocyanate groups and hydroxyl groups, i.e., the NCO content of compounds a) is less than 2 wt.%, preferably less than 0.5 wt.% and more preferably less than 0.2 wt.% and the hydroxyl group content is less than 1 wt.%, preferably less than 0.3 wt.% and more preferably less than 0.1 wt.%. This objective may be achieved during the preparation of these compounds by reacting the starting components at an NCO/OH equivalent ratio of 1.2:1 to 1:1.2, preferably of 1.1:1 to 1:1.1 and more preferably 1:1. The reaction to form urethane groups is generally carried out at a temperature of 20 to 130°C, preferably 50 to 90°C. The reaction is preferably carried out in the melt, although suitable organic solvents may be used.

Compounds a) may be prepared by reacting a polyol, preferably a diol, with a fluorine-containing monoisocyanate optionally in admixture with other monoisocyanates; by reacting a fluorine-containing polyol, preferably a diol, optionally in admixture with other polyols, with a monoisocyanate; by reacting a fluorinated polyisocyanate, preferably a diisocyanate, optionally in admixture with other polyisocyanates, with a monohydroxy compound; or by reacting a polyisocyanate, preferably a diisocyanate, with a fluorine-containing monohydroxy compound, optionally in admixture with other monohydroxy compounds.

In another embodiment of the present invention both of the compounds used to prepare compounds a) may contain fluorine. In addition, any of the preceding monofunctional compounds may be mixed with higher functional compounds, provided that the resulting urethane compounds are substantially free of isocyanate and hydroxy groups. The presence of these higher functional compounds results in chain extension, which introduces more urethane groups. If these urethane groups are subsequently converted to allophanate groups, the resulting products will have a higher isocyanate functionality.

Most preferably compounds a) are diurethanes prepared by reacting a diisocyanate with a fluorine-containing monohydroxy compound.

The isocyanates used for the production of the compounds a) containing urethane groups are selected from linear or branched aromatic or (cyclo)aliphatic mono-, di- and/or polyisocyanates having a molecular weight of 99 to 1000, preferably 99 to 400 and more preferably 140 to 300, and an NCO content of 10 to 60 wt.%, preferably 18 to 60 wt.% and more preferably 30 to 50 wt.%. The average NCO functionality of these isocyanates is 1 to 4, preferably 1 to 2 and more preferably 2.

Examples of monoisocyanates, which may be used alone or in admixture with di- or polyisocyanates to prepare the compounds containing urethane groups, include aromatic monoisocyanates such as phenyl isocyanate; (cyclo)aliphatic monoisocyanates having 4 to 18 carbon atoms such as n-butyl isocyanate, n-hexyl isocyanate, cyclohexyl isocyanate, n-stearyl isocyanate; and fluorinated aromatic or (cyclo)aliphatic monoisocyanates such as trifluoro-m-tolyl isocyanate and 2,4-difluorophenyl isocyanate.

Examples of suitable organic diisocyanates include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (isophorone diisocyanate or IPDI), 4,4' and/or 2,4'-dicyclohexyl-methane diisocyanate, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, xylylene diisocyanate,  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or 2,6-hexahydrotoluylene diisocyanate, 1,3- and/or 1,4-phenylene diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, 2,4- and/or 4,4'-diphenyl-methane diisocyanate, 1,5-diisocyanato naphthalene and mixtures thereof.

owing the formation of the allophanate groups. Monoisocyanates should be used, if at all, in only minor quantities because when they react with urethane groups, they result in non-functional allophanate groups, i.e., groups that do not contain isocyanate groups. The average functionality of component b) is 2 to 4, preferably 2.

The reaction of the urethane group-containing compound a) with polyisocyanate component b) is carried out at an NCO/urethane equivalent ratio of 3:1 to 100:1, preferably 6:1 to 60:1 and more preferably 8:1 to 30:1, and at a temperature of 50°C to 250°C, preferably 60°C to 150°C and more preferably 70°C to 120°C. Suitable methods for preparing allophanate group containing polyisocyanates are known and described in U.S. Patents 3,769,318, 4,160,080 and 4,177,342 and 4,738,991, the disclosures of which are herein incorporated by reference.

The allophanatization of compounds a) in the presence of polyisocyanates b) may be carried out in the absence or in the presence of solvents which are inert to isocyanate groups. Depending on the area of application of the products according to the invention, low to medium-boiling solvents or high-boiling solvents can be used. Suitable solvents include esters such as ethyl acetate or butyl acetate; ketones such as acetone or butanone; aromatic compounds such as toluene or xylene; halogenated hydrocarbons such as methylene chloride and trichloroethylene; ethers such as diisopropylether; and alkanes such as cyclohexane, petroleum ether or ligroin.

Instead of using catalysts that promote the formation of allophanate groups, it is also possible in accordance with the present invention to use catalysts that promote the formation of allophanate groups and isocyanurate groups. Suitable methods and catalysts for the preparation of polyisocyanates containing isocyanurate groups and allophanate groups are known and described in U.S. Patents 5,124,427; 5,208,334, 5,235,018, 5,290,902 and 5,444,146, the disclosures of which are herein incorporated by reference. The trimerization of the starting diisocyanate mixture may be carried out in the absence or in the presence of solvents which are inert to isocyanate groups, such as those previously described.

Examples of suitable catalysts include tetraalkylammonium hydroxides or arylalkylammonium hydroxides; metal salts such as iron(III) chloride or potassium octoate; zinc compounds such as zinc stearate zinc octoate, zinc naphthenate or zinc acetylacetone; tin compounds such as tin(II) octoate, tin(II) 2-ethyl-hexanoate; tin(II) laurate, dibutyltin oxide, dibutyltin dichloride, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate or dioctyltin diacetate; aluminum tri(ethyl acetoacetate); and compounds of manganese, cobalt or nickel and mineral acids such as trifluoroacetic acid, sulphuric acid, hydrogen chloride, hydrogen bromide, phosphoric acid or perchloric acid.

The catalysts are preferably added prior to the allophanatization reaction. While they may be added prior to the urethane formation, this is less preferred because of the possibility of forming allophanate groups, which would affect the stoichiometry of the urethane formation reaction. The catalysts are used in concentrations of 0.001 to 5 wt.%, preferably 0.005 to 1 wt.%.

At a temperature of about 50°C and in the presence of the required catalyst or catalyst solution the allophanatization reaction begins and is indicated by an exothermic reaction. When catalysts for the formation of allophanate groups and isocyanurate groups are present, it is possible to control the rate of formation of these two groups. As the reaction temperature increases the conversion rate of urethane groups to allophanate groups increases faster than the formation of isocyanurate groups. Accordingly, by varying the reaction temperature, it is possible to obtain different ratios of allophanate groups to isocyanurate groups.

The progress of the reaction is followed by determining the NCO content by a suitable method such as titration, refractive index or IR analysis. Thus, the reaction may be allowed to proceed to completion or it may be terminated at the desired degree of allophanatization. The allophanatization reaction is terminated after 50 to 100%, preferably 80 to 100% by weight, more preferably 90 to 100% by weight and most preferably 95 to 100% by weight of the urethane groups have been converted to allophanate groups. The polyisocyanate adducts should contain sufficient allophanate groups to ensure that the polyisocyanate adducts remain stable and homogeneous in storage for 3 months at 25°C. If the polyisocyanate adducts contain an insufficient number of allophanate groups, the product may be cloudy and a gradual settling of insoluble constituents may take place during storage.

The termination of the allophanatization and optionally trimerization reactions can take place, for example, by the addition of a catalyst poison, such as those disclosed in the previously discussed literature references. For example, when using basic catalysts the reaction is terminated by the addition of a quantity, which is at least equivalent to the catalyst quantity, of an acid chloride such as benzoyl chloride. When using heat-labile catalysts, for example, certain quaternary ammonium hydroxides, poisoning of the catalyst by the addition of a catalyst-poison may be dispensed with, since these catalysts decompose in the course of the reaction. The use of suspended catalysts is also possible. These catalysts are removed after achieving the desired degree of trimerization by filtering the reaction mixture.

The working-up of the reaction mixture, optionally after previous separation of insoluble catalyst constituents, may take place in various ways depending upon how the reaction was conducted and the area of application for the isocyanates. Any solvent used during the reaction and any unreacted monomer present in the polyisocyanate product may optionally be removed, e.g., by distillation, in known manner. The product obtained after the optional distillation step or after the reaction is allowed to proceed to completion generally contains a total of less than 2% by weight, preferably less than 1% by weight, more preferably less than 0.5% by weight and most preferably less than 0.2% by weight, based

component are selected to provide equivalent ratios of isocyanate groups (whether present in blocked or unblocked form) to isocyanate-reactive groups of about 0.8 to 3; preferably about 0.9 to 1.5.

To accelerate hardening, the coating compositions may contain known polyurethane catalysts, e.g., tertiary amines such as triethylamine, pyridine, methyl pyridine, benzyl dimethylamine, N,N-dimethylamino cyclohexane, N-methyl-piperidine, pentamethyl diethylene triamine, 1,4-diazabicyclo[2.2.2]-octane and N,N'-dimethyl piperazine; or metal salts such as iron(III)-chloride, zinc chloride, zinc-2-ethyl caproate, tin(II)-ethyl caproate, dibutyltin(IV)-dilaurate and molybdenum glycolate.

The products according to the invention are also valuable starting materials for one-component coating compositions, preferably polyurethane coating compositions, in which the isocyanate groups are used in a form blocked by known blocking agents. The blocking reaction is carried out in known manner by reacting the isocyanate groups with suitable blocking agents, preferably at an elevated temperature (e.g. about 40 to 160°C), and optionally in the presence of a suitable catalyst, for example, the previously described tertiary amines or metal salts.

Suitable blocking agents include monophenols such as phenol, the cresols, the trimethylphenols and the tert. butyl phenols; tertiary alcohols such as tert. butanol, tert. amyl alcohol and dimethylphenyl carbinol; compounds which easily form enols such as acetoacetic ester, acetyl acetone and malonic acid derivatives, e.g. malonic acid diethylester; secondary aromatic amines such as N-methyl aniline, the N-methyl toluidine, N-phenyl toluidine and N-phenyl xylidine; imides such as succinimide; lactams such as  $\epsilon$ -caprolactam and  $\delta$ -valerolactam; pyrazoles such as 3,5-dimethyl pyrazole; oximes such as butanone oxime, methyl amyl ketoxime and cyclohexanone oxime; mercaptans such as methyl mercaptan, ethyl mercaptan, butyl mercaptan, 2-mercaptopbenzthiazole,  $\alpha$ -naphthyl mercaptan and dodecyl mercaptan; and triazoles such as 1H-1,2,4-triazole.

The polyisocyanate adducts according to the invention may also be used as the polyisocyanate component in two-component water borne coating compositions. To be useful for in these compositions the polyisocyanate adducts must be rendered hydrophilic either by blending with external emulsifiers or by a reaction with compounds containing cationic, anionic or non-ionic groups. Methods for rendering the polyisocyanates hydrophilic are disclosed in copending application, U.S. Patents 5,194,487 and 5,200,489, the disclosures of which are herein incorporated by reference. The reduced surface tension of the modified polyisocyanate mixtures enhance pigment dispersion and substrate wetting.

The coating compositions may also contain other additives such as wetting agents, flow-control agents, leveling agents, skin inhibitors, anti-foaming agents, fillers (such as silica, aluminum silicate and high boiling waxes), substances for controlling the viscosity, pigments, dyes, UV absorbers and thermal and oxidative stabilizers. The coating compositions may be applied to the substrate to be coated in solution or from the melt by conventional methods such as painting, rolling, pouring, spraying, dipping or flow coating. Suitable substrates include wood, plastics, leather, paper, textiles, glass, ceramics, plaster, masonry, metals and concrete.

The coating compositions containing the polyisocyanate adducts according to the invention provide coatings which have good dry times, adhere well to a metallic base, and are particularly light-fast, color-stable in the presence of heat and very resistant to abrasion. Furthermore, they are characterized by high hardness, elasticity, very good resistance to chemicals, high gloss, good weather resistance, good environmental etch resistance and good pigmenting qualities. Above all, the coating compositions have an excellent surface appearance and excellent cleanability.

The invention is further illustrated, but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

#### EXAMPLES

##### Polyisocyanate 1 - Comparison

A biuret group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of about 23%, a content of monomeric diisocyanate of <0.7% and a viscosity at 25°C of 1300-2200 mPa.s (available from Bayer Corporation as Desmodur N 3200).

##### Polyisocyanates 2 and 3 - According to the invention

HDI and a fluorinated monoalcohol (available from 3M as Fluorad FC-10, MW 570) at an NCO/OH equivalent ratio of 1:1 were added to a 3-neck flask equipped with a gas bubbler, mechanical stirrer thermometer and condenser. Dry nitrogen was bubbled through the stirred reaction mixture while it was heated to 90°C. After 4 hours at 90°C, no free NCO groups remained as measured by IR. 10 equivalents, based on the equivalents of urethane groups present in the diurethane, of either HDI or IPDI were added to the diurethane, the resulting mixture was heated to 120°C and stannous octoate was added dropwise as catalyst. When the NCO content reached the desired value, the reaction was stopped by adding 1.0 equivalent (based on the catalyst) of di(2-ethylhexyl) phosphate. Excess diisocyanate monomer was removed from the resulting crude reaction mixture by thin film evaporation to provide the final product, which was diluted

Table 2

Ingredients		
1.	24.7 parts	of a polyester polyol (available as Desmophen 631A-75 from Bayer Corporation)
2.	39.1 parts	of titanium dioxide (available as Ti-Pure R-960 from Dupont)
3.	0.3 parts	of a grinding aid (available as Anti-Terra U from Byk Chemie)
4.	3.1 parts	of a cellulose acetate butyrate (available as CAB 551-0.01 from Eastman)
5.	1.0 part	of an anti-settling agent (available as MPA-2000X from Rheox)
6.	0.4 parts	of a 0.4% solution of dibutyltin dilaurate (available as Metacure T-12 from Air Products and Chemicals)
7.	8.4 parts	of a polyester polyol (available as Desmophen 670A-80 from Bayer Corporation)
8.	0.2 parts	of a tertiary amine catalyst (available as Desmorapid PP from Bayer AG)
9.	1.4 parts	of 2,4-pentanedione
10.	18.8 parts	of methyl n-amyl ketone
11.	2.6 parts	of diisobutyl ketone

Film Preparation

Component I was blended with the amounts of the components set forth in Table 3 (NCO/OH equivalent ratio 1.24:1; fluorine content 0.1%, based on the weight of the dried film). After mixing the composition was sprayed out to a 3 mil wet film thickness. The films were allowed to cure for two weeks at a constant temperature and humidity of 70°C and 55%. The surface energies of the resulting films are set forth in Table 3.

TABLE 3

Example	1	2	3 (Comp)
Component 1	73.4	73.4	73.5
Polyisocyanate 1	18	18	18.1
Methyl ethyl ketone	7.1	7.1	7.1
Methyl amyl ketone	1.3	1.3	1.3
Polyisocyanate 2	0.2	-	0
Polyisocyanate 3	-	0.3	0
Film Surface energy (Dynes/cm)	16.8	18.4	31.5

Surface Energy Measurements

All reported liquid (resin) surface energies (in dynes/cm) were obtained using the ring or Du Noüy method. In this static method, the force applied on a thin platinum ring was measured using a tensiometer.

All reported solid (coating) surface energies (in dynes/cm) were obtained by the Owens-Wendt procedure. The contact angle of two solvents (water and methylene iodide) were measured with a goniometer. Several readings were taken and averaged. The averages were then used to calculate the solid surface energy of the coating, taking into account the contributions of polar and dispersive forces.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

13. The polyisocyanate composition of Claim 12 wherein compound a) is prepared by reacting an aliphatic diisocyanate with a fluorine-containing compound containing one hydroxy group.
14. The polyisocyanate composition of Claim 12 wherein compound a) is prepared by reacting a monoisocyanate with a compound containing two hydroxy groups.
15. The polyisocyanate composition of Claim 13 wherein said aliphatic diisocyanate comprises 1,6-hexamethylene diisocyanate.
16. A process for the preparation of a polyisocyanate adduct containing allophanate groups, fluorine and optionally isocyanurate groups which comprises reacting a compound a) which
  - i) is substantially free of hydroxyl groups and isocyanate groups,
  - ii) has an average of at least two urethane groups per molecule and
  - iii) contains 0 to 50% by weight of fluorine, based on the weight of the polyisocyanate adduct,with an excess quantity, based on the equivalents of urethane groups, of a polyisocyanate b), which optionally contains fluorine, to form a polyisocyanate adduct and optionally removing at least a portion of the unreacted excess polyisocyanate b), provided that compound a) and polyisocyanate b) contain a total of at least 0.001% by weight, of fluorine, based on the weight of the polyisocyanate adduct.
17. A two-component coating composition containing the polyisocyanate adduct of Claim 1 and a compound containing at least two isocyanate-reactive groups.
18. A one-component coating composition containing the polyisocyanate adduct of Claim 1, in which the isocyanate groups are blocked, and a compound containing at least two isocyanate-reactive groups.

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